Supporting Information for:

Nanoelectrical and Nanoelectrochemical Imaging of Pt/p-Si Electrodes and Pt/p^+-Si Electrodes

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Experimental details:

Fabrication of electrodes for microscopic studies

The RCA 1 etching solution contained 5:1:1 by volume of H_2O : H_2O_2(aq) (30%) : conc. NH_4OH (28%). The RCA 2 etching solution contained 5:1:1 by volume of H_2O : aq H_2O_2 (30%): conc. HCl(aq) (37%) and was maintained at 75 ^oC. The solution for electroless deposition of Pt consisted of 1 mM H_2PtCl_6(aq) in 0.50 M HF(aq). A diamond scribe was used to scratch a Ga/In eutectic mixture (Aldrich) onto the back side of each Pt/p-Si chip. For AFM studies, 1.0 x 1.0 cm chip samples were mounted onto an SPM sample-mounting disk (SD-101, Bruker) using Ag paint (SPI, Inc.), and allowed to dry overnight. For PF-SECM measurements, a 3.8 x 3.8 cm p^+-Si chip was loaded onto a flat Cu foil of the same size, instead of a sample-mounting disk.

Characterization of deposited Pt nanoparticles

Peak Force tapping mode (PFT): In PFT mode, the probe was sinusoidally modulated at a low, off-resonance frequency. The frequency was 1 or 2 kHz with an amplitude of 100 or 150 nm. The feedback signal in PFT was the maximum force between the tip and the sample during every tapping cycle. The tip intermittently contacted the surface for ~ 100 to 300 μs. For surface topography mapping, ScanAsyst-air probes (Bruker) with a nominal tip radius of 2 nm were used. The surface was scanned using a relatively rapid line scan (left to right) while slowly moving the tip in the orthogonal direction (vertical in the plotted figures). Generally only data from the reverse scan direction (right to left, retrace) was used.

Peak-Force Tunneling AFM (PF-TUNA) mode: To capture current signals under an applied sample bias, an electronic module with a bandwidth of 10–20 kHz was used.[1] The PF-TUNA software algorithm allowed capture of currents during the period of maximum contact force, averaged over the contact duration (contact current), and averaged over the whole tapping cycle (TUNA current). The conductive probes used were SCM-PIT probes from Bruker with Pt/Ir coating layers and nominal tip radii of 20 nm. The imaging force was 5 – 10 nN.

For moving the particles in air, the Nano-Manipulation (NanoMan) software package was used with a TESPA probe (Bruker, nominal spring constant 40 N/m). After the sample was imaged using AFM conventional tapping mode, a script was written to control subsequent tip movements to push a particle. When pushing a particle, the tip stopped oscillation and maintained a 10 nm distance above the substrate surface while moving across the particle from left to right. When the script was complete, the same area of the surface was re-imaged using conventional tapping mode.

Peak-Force Scanning Electrochemical Microscopy (PF-SECM): PF-SECM was used for local, in situ electrical and electrochemical measurements using commercially available nanoelectrode probes from Bruker. The probes were fully coated by SiO_2 except for the Pt conical tip apex with a height of ~200 nm and an end tip diameter of ~50 nm. The detailed electrochemical characterization of these probes has been reported

previously.[2] Electrochemical studies by PF-SECM were performed using an aqueous electrolyte solution of 10 mM $[Ru(NH3)_6]]^{3+}$ and 0.1 M KCl. The electrochemical cell had a Pt wire counter electrode and a AgCl-coated Ag wire as a quasi-reference electrode (AgQRE). A CHI760 bipotentiostat (CH Instrument, Texas) was used to control the electrochemical conditions. The probes were briefly tested by running a few cyclic voltammograms at a scan rate of 50 mV/s in the AFM electrochemical cell (Bruker). The surface area of the nanoelectrode probe was ~10^{-9} cm^2.[2] A typical particle in the SECM image (Figure 4) had an apparent size of ~ 140 x 180 nm. If the particle is treated as a sphere of 160 nm, the surface area is ~10^{-9} cm^2. Thus when the AFM-SECM tip was in contact with a particle on the surface, the active area for $[Ru(NH_3)_6]]^{3+}$was approximately doubled.

In PF-SECM, the bipotentiostat was used in a 4-electrode scheme, in which the nanoelectrode AFM probe and the sample were working electrodes that shared the same reference and counter electrodes. For SECM imaging, the probe moved in an interleaved scan (PFT and SECM) pattern. First a forward and backward line scan (main scan) in PFT imaging mode captured the topographical profile. The topographical data were stored for use in the second, or lift, forward and backward line scan. During the lift scan, the tip did not oscillate and followed the stored topographical line profile at a defined height above the sample surface. In the lift scan, as in PFT, only the back or retrace scan data were used. The lift height was 100 nm. Electrochemical information was captured during the lift scan. In the SECM scan the tip was biased at -0.4 V vs AgQRE to reduce the $[Ru(NH_3)_6]^{3+}$, while the sample was held at -0.1 V vs AgQRE to reoxidize the $Ru(NH_3)_6]^{2+}$ generated by the AFM tip. Approaching the tip to a highly resistive region on the surface where $[Ru(NH_3)_6]^{2+}$ is not reoxidized led to a reduction in tip current (negative feedback). For a conductive region where $[Ru(NH_3)_6]^{3+}$ was regenerated, a positive feedback was observed.[2a] These distinct responses allowed imaging the inhomogeneity of the conductance on the sample surface. Before SECM mapping, the approach curve (tip current vs tip-sample distance) of the nanoelectrode probe was measured on a particle-free region of the surface. The tip was biased at -0.4 V vs AgQRE.

During the PFT part of the PF-SECM scan, the conductivity of the sample was also measured. When the tip was in contact with a conductive species, two processes gave rise to an increased current. The nanoparticle can act as an enlarged SECM electrode and thus produce an increase in the Faradaic current. Also, the voltage difference between the tip and the sample can produce an electrical current during tip-sample contact. During the scan, the tip is in contact with the surface for only part of the tapping cycle, ~80 µs for a 500 µs tapping period (2 kHz tapping frequency, 0.5 ms/cycle). The captured current was acquired by the bipotentiostat and routed to the AFM controller for processing into an image, yielding the tapping-cycle-averaged current measured in the PF-SECM scan that is denoted herein as the tip-contact current. The actual contact current is thus ~ 6 times (500/80) the tapping-cycle-averaged current.

Resistance Measurements

p-Si resistance: $R = \rho \frac{l}{A} = 7.5\Omega \cdot cm \times \frac{0.05cm}{1cm^2} = 0.375\Omega$

Pt particle (50 x 50 x 50 nm) resistance: $R = \rho \frac{l}{A} = 1.1 \times 10^{-7} \Omega \cdot m \times \frac{50 \times 10^{-9} m}{50 \times 10^{-9} nm \times 50 \times 10^{-9} nm} = 2.2\Omega$

Pt/Ir tip resistance*:* ~10 Ω from vendor

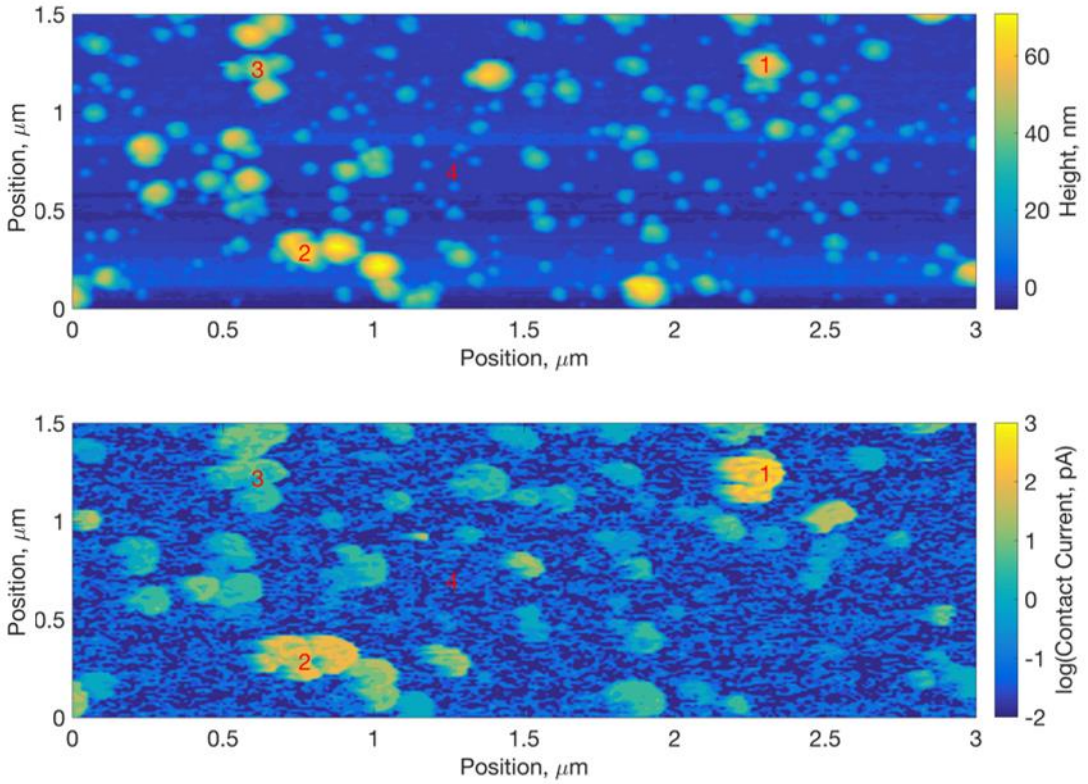

Fig S1. PF-TUNA scan of the same region of the Pt-NP/p-Si surface at 0.3 V shown in Figure 1 of the main text. (top) Contour plot of the surface topography after flattening; (bottom) Logarithm of the absolute value of the current. Note that the larger particles showed contact currents, and notice that the observed currents varied by a factor > 1000. Replotted from Fig 1AB to more clearly show the variance in scale.

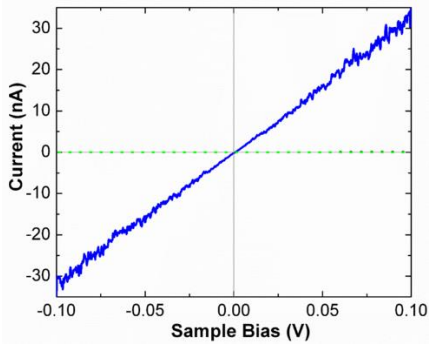

Figure S2. Expanded plot for Figure 1E from the main text. *I-V* data (blue solid line) captured from the Pt-TF/p-Si sample. The resistance obtained from the data was $3 \times 10^6\,\Omega$.

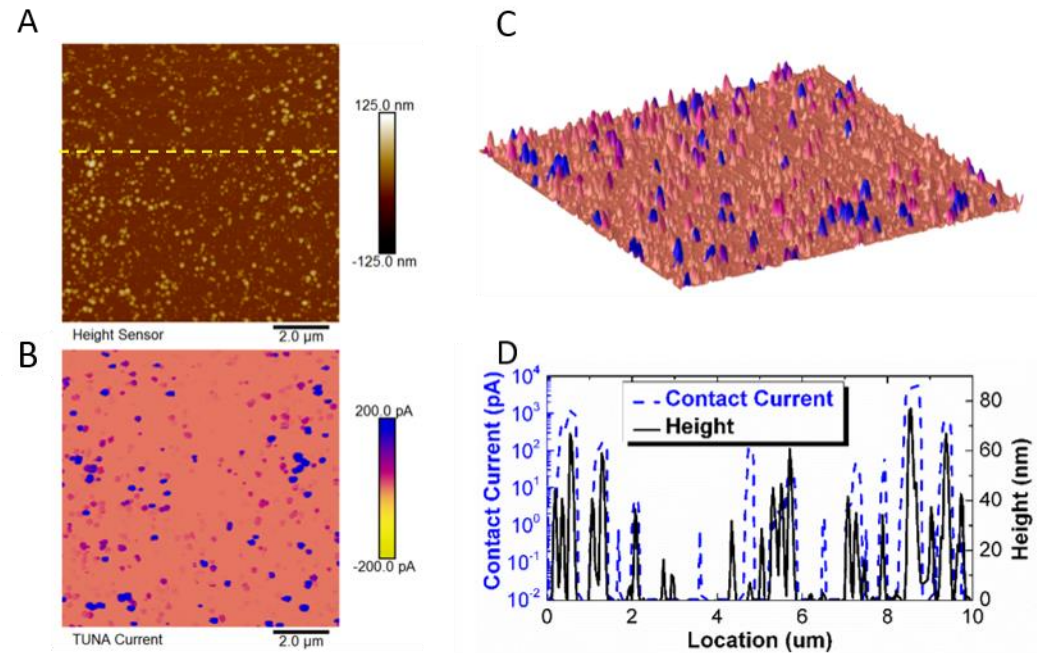

Figure S3. Topography and TUNA current for Pt nanoparticles electrolessly deposited onto a p- Si substrate captured by PF-TUNA. (A) Surface topography; (B) TUNA current at a sample bias of 0.5 V; (C) The 3-D rendering of the surface topography painted by the false-color current map; and, (D) Cross-sectional analysis of the surface topography (solid grey) and TUNA current (dashed blue) at the same sample location as indicated by the yellow dashed line in (A). As shown in Figure 1, the contact currents varied from the detection limit of <1 pA to 10^3 pA (Figure S1). Figures S1 and S3 both show this same amount of variation. The line profile plot in Figure 1D only shows currents < 40 pA, because the line was not drawn through any high current points, as shown in Figure 1B.

Table S1. Apparent mean diameters of the particles in Figure 3A and 3B of the main text before and after Nanoman pushing.

	Before NanoMan (nm)	After NanoMan (nm)	Increment
Ensemble	368	402	9.2%
#1	558	598	7.2%
#2	648	743	14.7%
#3	412	458	11.1%

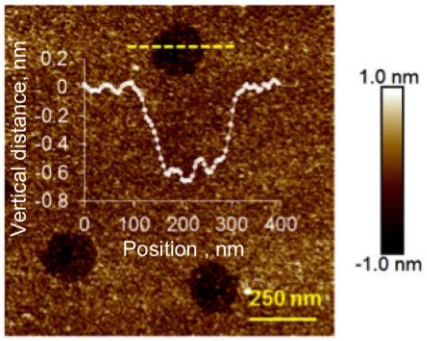

Figure S4. Indentations remaining on the Si surface after the particles were moved away by the SECM probe in 0.1 M KCl(aq). The on-image plot is a cross-sectional analysis of the line profile across a hole as indicated by the yellow dashed line.

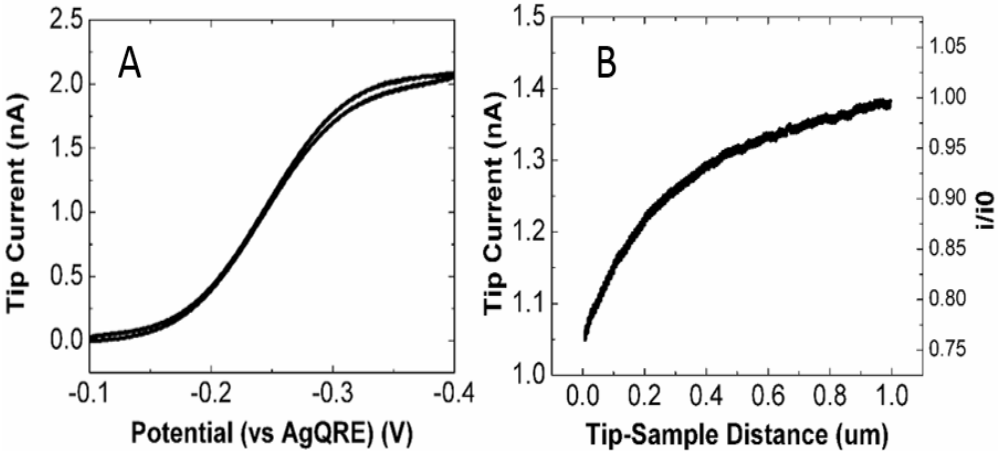

Figure S5. Electrochemical performance of a nanoelectrode probe used for PF-SECM imaging. (A) Two cyclic voltammograms measured in 10 mM $[Ru(NH_3)_6]^{3+}$ and 0.1 M KCl (aq) at a scan rate of 50 mV/s. A Pt wire was used as the counter electrode and a Ag wire coated with AgCl was used as the quasi-reference (AgQRE) electrode. (B) Approach curve (tip current vs tip-sample distance) captured under the same electrochemical conditions through force ramping the SECM probe at a triggered force of 10 nN and a ramp rate of 0.25 Hz. The normalized current is shown on the right ordinate axis.

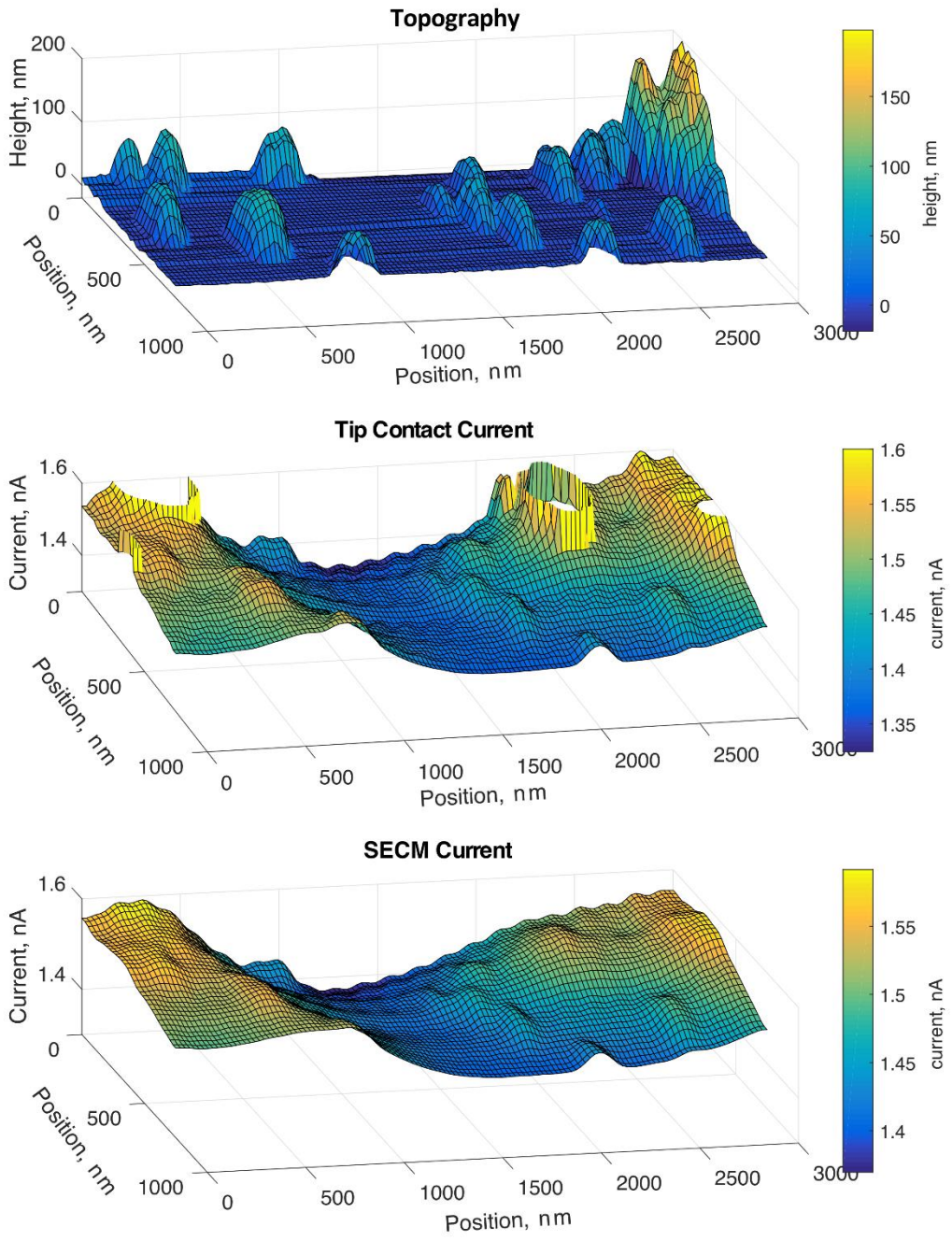

Figure S6. Same PeakForce SECM scans as shown in Figure 5 of the main text for Pt nanoparticles electrolessly deposited onto a degenerately doped p^+- Si substrate and measured in contact with 10 mM

$[Ru(NH_3)_6]^{3+}$ in 0.1 M KCl(aq). (top) Topography of the surface; (middle) Plot of the tip contact current truncated at 1.6 nA; (bottom) Plot of the SECM current.

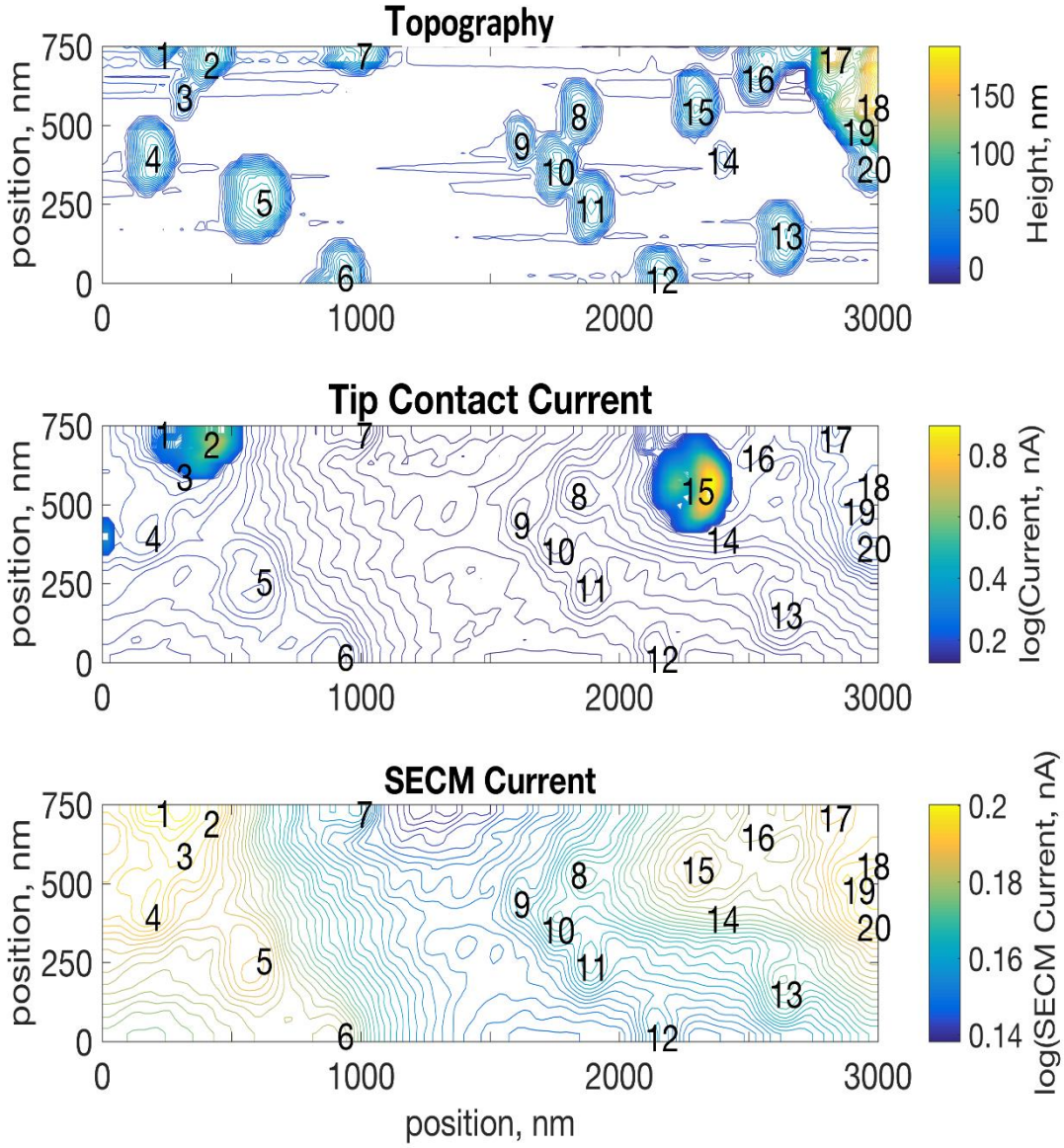

Figure S7. Same PeakForce SECM scans shown in Figure 4 of the main text for Pt nanoparticles electrolessly deposited onto a degenerately doped p^+- Si substrate and measured in contact with 10 mM $[Ru(NH_3)_6]^{3+}$ in 0.1 M KCl(aq). (top) Contour plot of the topography of surface; (middle) Contour plot of the common logarithm of the tip contact current; (bottom) Contour plot of the common logarithm of the SECM current.

[1] C. Li, S. Minne, B. Pittenger, A. Mednick, *Bruker Application Notes* **2011**, *132*, 1-12.

[2] a) Z. Huang, P. De Wolf, R. Poddar, C. Li, A. Mark, M. R. Nellist, Y. Chen, J. Jiang, G. Papastavrou, S. W. Boettcher, C. Xiang, B. S. Brunschwig, *Microscopy Today* **2016**, *24*, 18-25; b) M. R. Nellis, Y. Chen, A. Mark, S. Gödrich, C. Stelling, J. Jiang, R. Poddar, C. Li, R. Kumar, G. Papastavrou, M. Retsch, B. S. Brunschwig, Z. Huang, C. Xiang, S. W. Boettcher, *Nanotechnology* **2017**, *28*, 095711.